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Anthraquinone-derivatised carbon powder: reagentless voltammetric pH electrodes

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Abstract

A simple pH probe is developed based upon the covalent chemical derivatisation of carbon particles with anthraquinone. The amperometric response of electrodes constructed from this material is examined and shown to produce a Nernstian linear response to pH from 1 to 9, over a range of temperatures from 20 to 70 °C, consistent with a two-electron, two-proton electrochemical process.

Keywords: Anthraquinone; pH measurement; Derivatised carbon; High temperature

1. Introduction

The sensing of pH in solution is one of the most common analytical measurements performed within both academic and industrial applications.

The most common systems for pH sensing are based upon either potentiometric or amperometric devices [1]. The usual potentiometric approach utilises the glass electrode [2,3] due to its simplicity of handling and low sensitivity to many potential interferents within the solution to be measured. Other devices include ion-selective membranes [4,5], ion-selective field effect transistors [3,6], two-terminal microsensors [7] as well as optical [8] and conductometric [9] pH-sensing devices. However, these types of devices can often suffer from instability and/or drift and therefore require constant recalibration [10].

The majority of amperometric sensors are based upon the pH-switchable permselectivity of membrane or films on the electrode surface [11–15]. For example, recent work by Stred'ansky et al. [10] has focused on the use of various pH-sensitive redox-active compounds as a means of designing a

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suitable amperometric probes, which are based upon pH-changing enzymes. In these cases, the probe is held at a set potential and the current is measured such that the pH local to the electrode surface can be monitored.

In the work outlined below, we develop a pH probe based upon the redox activity of the anthraquinone species. Initially, the work describes the derivatisation of a carbon particle by anthraquinone. This is carried out by chemical as opposed to the electrochemical reduction of anthraquinone-1-diazonium chloride in the presence of carbon powder. The voltammetry of these derivatised particles is shown to be consistent with that of a covalently attached species and produces a linear Nernstian response from pH 1 to 9 over a temperature range 20–70 °C. As such the derivatised carbon could foreseeably be utilised for a pH sensor in a variety of applications.

2. Experimental

2.1. Reagents and equipment

Unless otherwise stated all reagents were obtained from Aldrich and were of the highest grade available and used without further purification. All solutions and subsequent dilutions were carried out using deionised water from Elgastat (Elga, UK) UHQ grade water system with a resistivity of not less than 18 MΩ cm.

Electrochemical measurements were recorded using a PalmSens potentiostat (Houten, The Netherlands) controlled by an iPAQ H3760 pocket computer (Compaq, US) with a standard three-electrode configuration. All experiments were carried out in a three-armed cell of volume 30 cm^3. A basal plane pyrolytic graphite (bppg, 0.20 cm^2) electrode acted as the working electrodes (see below). A platinum electrode acted as the counter-electrode, and a saturated calomel as the reference electrode (SCE, Radiometer, Copenhagen) completed the cell assembly. Unless otherwise stated all square wave measurements were recorded using the following parameters: frequency, 25 Hz; step potential, 2 mV; and amplitude, 25 mV.

High-temperature voltammetry was undertaken using a double-wall glass cell thermostated at an appropriate temperature through the circulation of water from a heated bath.

Scanning electron microscopy (SEM) was conducted using a Cambridge stereoscan electron microscope at a magnification of 83 ×.

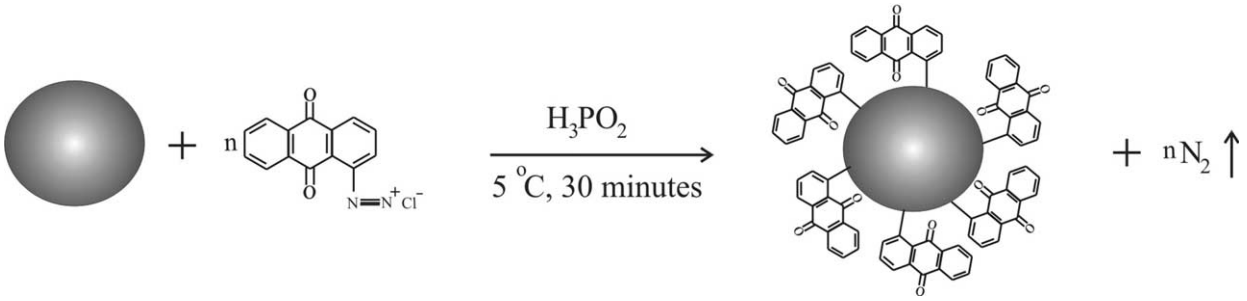
2.2. Derivatisation of carbon powder with anthraquinone

Initial characterisation of the size of the carbon particles used SEM. This was carried out by attaching the carbon particles to a strip of conducting sticky tape, from which SEM image was taken. Analysis of the image revealed that the carbon particles had a mean diameter of 1.5 μm, consistent with that stated by the manufacturer (Aldrich, graphite powder, 1–2 μm, synthetic) (Scheme 1).

Initially, 2 g of carbon powder was mixed with a 10 cm^3 solution containing 5 mM Fast Red AL Salt (anthraquinone-1-diazonium chloride) (Acros Organics), to which 50 mM hypophosphorous acid (H_3PO_2, 50%; Aldrich) was added. This solution was then left to stand at 5 °C for 30 min with occasional stirring at regular intervals (every 10 min). After which the solution was filtered by water suction in order to remove any unreacted species from the carbon surface. Further washing with deionised water was carried out to remove excess acid and finally with acetonitrile to remove any unreacted diazonium salt in the mixture. The carbon particles were then air-dried by placing inside a fume hood for a period of 12 h after which they were stored in an airtight container.

2.3. Immobilisation onto basal plane pyrolytic graphite

The newly derivatised anthraquinone carbon powders (AQcarbon) were characterised by abrasive immobilisation [16–20] onto the surface of a bppg electrode prior to characterisation. This was done by initially polishing the electrode on glass polishing paper (H00/240) after which they were polished on silicon carbide paper (P1000C) for smoothness. The derivatised carbon was then



Scheme 1. Homogeneous derivatisation procedure of carbon by anthraquinone-1-diazonium chloride.

mechanically immobilised onto the bppg electrode by gently rubbing the electrode surface on a fine qualitative filter paper (Whatman) containing the functionalised carbon. A schematic diagram of the resulting modified surface is shown in Fig. 1.

3. Results and discussion

3.1. Characterisation of AQcarbon

The cyclic voltammetric response of AQcarbon immobilised on a bppg electrode in a pH 7 buffer (0.1 M phosphate + 0.1 M KCl) solution at various scan rates (50–1000 mV s^{-1}) are detailed in Fig. 2. A reduction wave is initially observed at −0.56 V (vs SCE) with a corresponding oxidation peak at −0.50 V (vs SCE). A plot of reduction peak current against scan rate (not shown) was observed to be linear over the scan rates studied and is consistent with the derivatisation of the carbon powder by the anthraquinone species such that the voltammetry is indeed originated from an immobilised species.

In order to further verify that the anthraquinone is attached to the carbon particles, the buffer solution was replaced after the above scan rate experiment had been carried out and the voltammetric response recorded. The corresponding voltammetric response (not shown) was found to overlay that of the last voltammogram recorded in the former buffer solution thereby confirming that

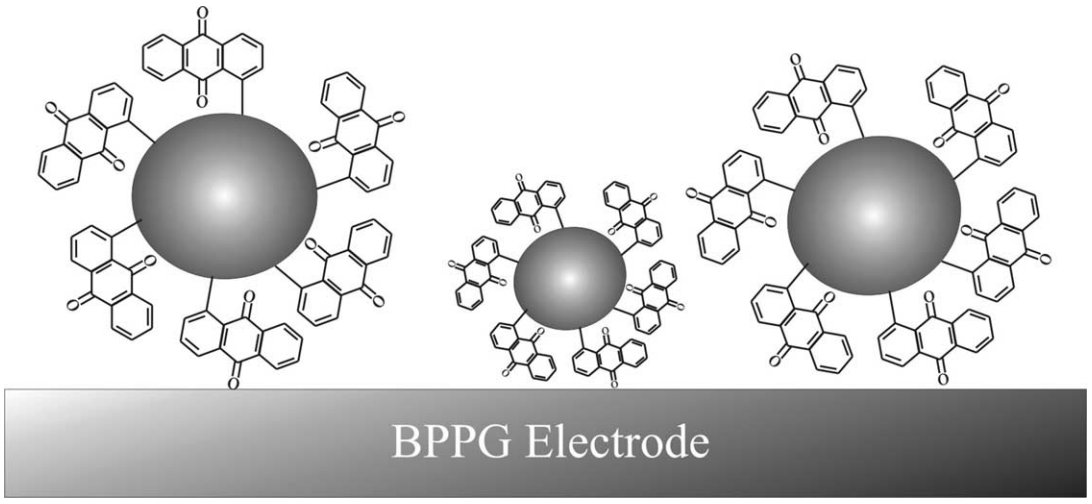


Fig. 1. Schematic diagram of the immobilised anthraquinone-derivatised carbon powder on a bppg electrode.

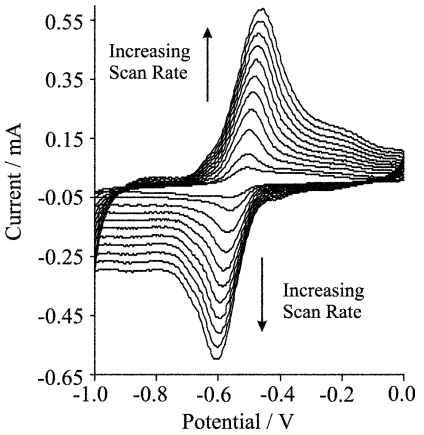


Fig. 2. Voltammetric response of AQcarbon (pH 7, 0.1 M phosphate+0.1 M KCl) immobilised on bppg at various scan rates (50, 100, 200, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1}).

the anthraquinone species is attached to the carbon particles, therefore, corroborating the scan rate results detailed above.

In order to provide evidence that this carbon can be used as a suitable pH probe, the voltammetric response of AQcarbon was examined over a pH range from 0 to 13 both at room temperature and elevated temperatures up to 70 °C.

3.2. Voltammetric response of AQcarbon at 23 °C from pH 0 to 13

In all studies detailed below, square wave voltammetry [21] was utilised as the electrochemical probe of the system. This has significant advantages to conventional cyclic voltammetry, as it provides a means of carrying out a single sweep which produces a well-defined voltammetric peak due to the reversibility of the anthraquinone system [22] and can therefore aid in the resolution of AQcarbon reduction wave especially at higher pH where oxygen reduction competes at similar potentials. The corresponding square wave voltammograms were recorded for the immobilised AQcarbon in a range of pH solutions (pH 4.6, 0.1 M acetic acid+0.1 M sodium acetate buffer; pH 6.8, 0.025 M disodium hydrogen phosphate+0.025 M potassium dihydrogen phosphate buffer; pH 9.2, 0.05 M disodium tetraborate buffer) and are overlaid in Fig. 3a. These show that as the pH increases, the peak potential shifts towards more negative values thereby making the reduction of the AQ species more difficult as is expected. The voltammetric responses reveal that for each pH studied a slight shoulder is observed at a higher potential on each of the voltammetric waves. The presence of this shoulder can be tentatively attributed to the intermediate electrochemical reduction of the quinone to a semi-quinone species.

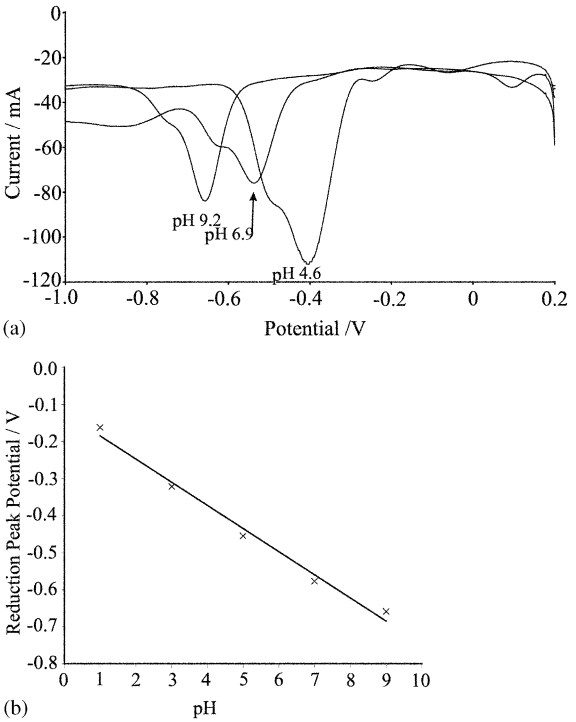


Fig. 3. (a) Square wave voltammograms detailing the effect of pH on AQcarbon signal at pH 4.6 (0.1 M acetic acid+sodium acetate buffer), pH 6.8 (0.025 M disodium hydrogen phosphate+0.025 M potassium dihydrogen phosphate buffer) and pH 9.2 (0.05 M disodium tetraborate buffer). (b) A plot of reduction peak potential against pH for AQcarbon immobilised on bppg.

The corresponding plot of reduction peak potential against pH for the main reduction wave for the five different pH values studied is given in Fig. 3b. This reveals a linear response from pH 1 to 9 with a corresponding gradient of ca. 58 mV

per pH unit which is consistent with an n-electron, m-proton transfer, where n and m are likely to be equal to 2, consistent with studies of anthraquinone derivatives at mercury electrodes [23,24].

3.3. Voltammetric response of AQcarbon at elevated temperature from pH 0 to 13

In order to show that the freshly derivatised AQcarbon might be used as a suitable pH probe, the effect of temperature on the peak potential and its variation with pH were studied. Analysis of Nernst equation (1) shows that as the temperature increases, the gradients of the potential against pH plot should increase.

$$E_{1/2} = E^{0'} - \frac{2.3RTm}{nF}\ \text{pH} \qquad (1)$$

where $n = m = 2$. The theoretically calculated values for the gradient of the reductive peak potential against pH plot for a range of temperatures are detailed in Table 1. A second factor to be noted whilst studying the effect of temperature on the AQ reduction wave is how the pH of the solution will vary with temperature, as the dissociation constants of the components of the buffer solutions vary as the temperature is changed. Therefore, four IUPAC standard buffers (pH 1.5, 4.6, 6.2 and 9.2) were utilised in these studies which have a known pH at a set of temperatures [25].

The corresponding square wave voltammograms obtained in both pH 4.6 (acetate buffer) and pH 9.2 (borax buffer) over a range of temperatures from 20 to 70 °C are detailed in Fig. 4a and b, respectively. As can be seen from the voltammograms, as the temperature is raised the peak currents increase in magnitude in both cases as expected due to increased rate of the reduction process. Analogous experiments were carried out at pH 1 and pH 7 with the square wave voltammograms (not shown) producing similar responses whereby the peak currents increased with temperature.

Table 1
A comparison of the theoretically predicted gradient and experimentally obtained gradient for the plot of pH against peak potential for a range of temperatures from 20 to 70 °C

Temperature (°C)	Theoretical shift (mV per pH)	Experimental shift ±5% (mV per pH)
20	58.1	57.9
30	60.1	61.0
40	62.1	62.7
50	64.1	65.3
60	66.1	65.9
70	68.1	70.1

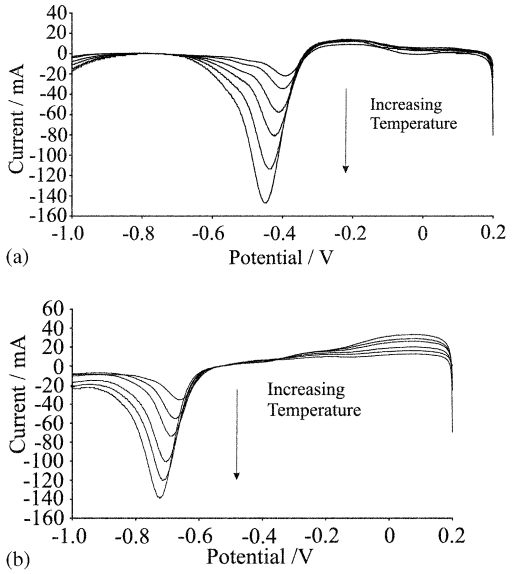


Fig. 4. The square wave voltammetric response of AQcarbon at various temperatures (20, 30, 40, 50, 60 and 70 °C) in (a) pH 4.6 (0.1 M acetic acid + 0.1 M sodium acetate) and (b) pH 9.2 (0.05 M disodium tetraborate) buffer solutions.

Analysis of the peak potential as a function of pH at each temperature is detailed in Table 1 which depicts how the gradient of pH against peak potential plot varies with temperature. These are compared with those predicted theoretically from the Nernst equation for a two-electron, two-proton transfer process. The data show a good agreement between the experimental and theoretically predicted values, thereby showing that the derivatised AQcarbon might easily be used as a basis for a simple, inexpensive pH probe which works over a wide range of temperatures.

The effect of the introduction of metal ions on the reduction peak potential of the AQ species was next examined. Both Mg^{2+} and Ca^{2+} are known to complex various anthraquinone species [26] and as such may affect the reduction peak potential. However, it was found that the addition of both calcium and magnesium chloride (0–1 mM) to the solution (pH 7 phosphate buffer) had no effect on the reduction potential of the AQ species. This can be attributed to the poor chelating properties of the chosen compound.

Furthermore, the effect of adding a surfactant (Triton X, 100 μl in 25 ml) to the solution was studied. The corresponding voltammetric response revealed no change in the reduction peak potential of the AQ species; however, a decrease in the reduction peak current was observed and can be attributed to the fouling of the electrode surface by the surfactant. Overall, these results show that AQcarbon acts as a pH probe over a wide range of temperature (20–70 °C) in the presence of both metal ions and surfactants.

4. Conclusion

Outlined above is a simple process which can be used to determine the pH of a solution. The homogeneous derivatisation of carbon with anthraquinone has been shown to occur, with the resulting voltammetric response of the derivatised material being that of a species attached to the carbon surface. The resulting peak potential data were shown to produce a linear response from pH 1 to 9 with a slope of ca. 58 mV per pH unit at 20 °C. The effect of temperature on the peak potential was also studied over the entire pH range and was found to be Nernstian from 20 to 70 °C. Furthermore, the stability of the response was shown in the presence of both complexing metal ions and surfactants.

Overall, these results proffer the leading to an amperometric pH probe whereby the derivatised carbon can be impregnated into a screen-printed electrode, producing a cheap and simple to use pH sensor.

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